

## **COAL/OIL COPROCESSING MECHANISM STUDIES**

by

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### **ABSTRACT**

Initial coprocessing studies, performed to provide a basis for larger scale tests of coprocessing options using batch one-liter autoclave and continuous hydrotreater facilities at PETC, are described. Areas investigated included the response of coal and petroleum resid combinations to processing under thermal hydrotreatment conditions, the means of increasing the conversion of coal, and the nature of resid demetalation effects. The petroleum resids possessed rather low donable-hydrogen capacities, and the interactions between the resids and coals are weak with respect to promoting formation of liquid products under thermal conditions. Maya ATB was superior to Boscan ATB or North Slope VTB for the conversion of Illinois No. 6 coal to liquid or soluble products. The Maya ATB/Illinois No. 6 coal system responded favorably to the addition of low concentrations of a highly dispersed, unsupported molybdenum catalyst. Extensive demetalation of the liquid product was observed and was a function of the amount of coal added. Results obtained using different coal and resid combinations, under thermal and catalytic conditions, and in the presence of various additives, imply that an absorptive mechanism is operative. The primary interactions leading to demetalation appear to be between the metal complexes of the resid and the insoluble carbonaceous coal-derived material. Demetalation of the liquid product was not observed to be dependent on conversion of the organically complexed metal in the resids to inorganic form.

### **INTRODUCTION**

The rapid consumption of conventional light petroleum reserves and the increasing need to refine lower quality petroleum feedstocks have recently prompted serious consideration of technology for coprocessing coal with petroleum resids or heavy bitumens. Coprocessing is attractive as a possible route for introducing the processing of coal in an evolutionary manner into existing refinery infrastructures without immediately incurring the large capital investment associated with other coal liquefaction alternatives.

An experimental program was initiated at PETC to obtain fundamental data on the coprocessing of coal with petroleum resids and to achieve a understanding of the observed "synergistic" interactions between coal and petroleum resid feedstocks.<sup>1-4</sup> This work has focused on coprocessing of Illinois No. 6 bituminous coal and, to a lesser extent,

Wyodak subbituminous coal with petroleum resids having widely different properties and coprocessing characteristics. Areas that have been investigated are the response of different coal and resid combinations to processing under thermal hydrotreatment conditions, the means of improving liquid product yields and coal conversions, and the extent and mechanism of liquid product demetalation.

## EXPERIMENTAL

Most of the coprocessing experiments were performed with Illinois No. 6 hvBb coal (>100 mesh) from the Burning Star Mine. A few comparative experiments were carried out with Wyodak subbituminous coals from the Clovis Point or Sarpy Creek Mines. The Clovis Point coal was dried before use. Proximate and ultimate analyses of the feed coals are given in Table 1.

Three petroleum resids were employed: North Slope VTB (950°F<sup>+</sup>), Boscan ATB (650°F<sup>+</sup>), and Maya ATB (650°F<sup>+</sup>). Analyses of these resids are presented in Table 2.

Selected experiments also employed a coal-derived thermal resid, pyrite, activated carbon, and kaolin.

Experiments were carried out in 42-mL shaker bomb microautoclave reactors. In the coprocessing experiments, a coal and a resid were added separately to the reactor. Any additive used was introduced after the coal and resid. After pressure testing, the reactors were charged with the reducing gas and slowly heated to run temperature, usually at a rate of ca. 8°C/min. Heating was achieved by immersion of a bank of five reactors into an electrically heated sand bath. Most experiments were performed with a feed coal concentration of 0-30 wt%, a cold charge pressure of 1200 psig, a reaction temperature of 425°C, and a reaction time of one hour.

The products were removed from the microautoclave reactors and separated into five fractions for analysis according to the scheme presented in Figure 1. The product work-up scheme minimizes the interactions between solvents and liquid products to reduce product contamination by solvent and product losses associated with solvent removal.

Yields of heptane solubles and THF solubles were calculated on the basis of dry weight of the recovered insolubles. Calculated coal conversions of THF solubles are based on maf coal after correcting for the contribution of the petroleum resid to the THF insolubles found in runs with no added coal.

## RESULTS AND DISCUSSION

### Effect of Coal Addition

The interaction of the petroleum resids with Illinois No. 6 bituminous coal under thermal-processing conditions was evaluated in terms of yields of heptane solubles, and coal conversions to THF solubles were evaluated as a function of coal addition. A limited number of experiments were performed with the Wyodak coal for comparative purposes.

The observed changes in heptane-soluble yields with increasing addition of coal to North Slope, Boscan, and Maya resid are shown in

Figures 2,3, and 4, respectively. The lower dashed line in these plots indicates the result expected if the coal simply acted as an insoluble diluent. The results for the North Slope VTB in Figure 2 do not deviate significantly from this line. However, an enhanced yield of heptane solubles is obtained with coal addition to both Boscan ATB and Maya ATB, as described by the upper solid curve (actual experimental results) in Figures 3 and 4. The effect is larger for the Maya ATB than for the Boscan ATB.

Interpretation of the enhanced yields requires knowledge of the relative contributions of the coal vs. resids to the heptane-soluble products. Since the petroleum resids are low in oxygen (if dry) and virtually free of phenolic functionality, relative contributions of coal to soluble product fractions can be monitored following the concentration of phenolic OH. As shown in Figure 5, there is a nearly linear increase of phenolic OH in the heptane solubles with coal addition regardless of resid. The data indicate a relatively weak interaction between Illinois No. 6 coal and the three petroleum resids.

Calculated coal conversions of Illinois No. 6 to THF solubles as a function of coal addition to North Slope VTB, Boscan ATB, and Maya ATB are summarized in Figure 6. The experimental results with coal concentrations less than 10 wt% are highly suspect owing to the small quantity of coal and THF insolubles. However, the remaining results indicate decreasing coal conversions to THF solubles with coal addition upon coprocessing with either North Slope VTB or Boscan ATB. In contrast, about 70% coal conversion was achieved in coprocessing with Maya ATB over the entire range of coal additions.

Based upon a number of reports indicating significant improvements in coal conversion by adding  $H_2S$  to the initial reducing atmosphere,<sup>5-7</sup> the effect of  $H_2S$  addition in coprocessing Illinois No. 6 coal with Boscan ATB and Maya ATB was examined. The results in Table 3 indicate a significant increase (10-15%) in coal conversion to THF solubles with added  $H_2S$ . There is also some improvement in the yield of heptane solubles, although the effect is largely masked by the already large contribution to the heptane solubles from the petroleum resid.

The response of the Illinois No. 6 coal and Maya ATB coprocessing system to addition of an active, highly dispersed, unsupported transition metal catalyst is also shown in Table 3. Molybdenum was added directly into the feed slurry in the form of an aqueous (ca. 12 wt%) solution of ammonium heptamolybdate. Hydrogen sulfide was added to the reducing atmosphere to insure rapid conversion of the molybdenum to the sulfide. Using 1.0% Mo gave virtually complete coal conversion to THF solubles and high heptane-soluble yields of ca. 80 wt%. Similar results were obtained using a catalyst concentration of 0.1 wt% Mo.

#### Metals Removal

One of the most attractive aspects of coprocessing is the potential of processing metal-rich petroleum resids with coal to yield a liquid product of significantly lower metal content. Such resids are currently difficult or impractical to process owing to the detrimental effects of these metals, particularly nickel and vanadium, on conventional upgrading catalysts.<sup>8,9</sup> The role of coal in promoting this demetalation has been investigated by a twofold approach involving monitoring the relative metal (Ni,V) content of the filtered liquid coprocessing

products by X-Ray fluorescence and monitoring the organic vanadium (vanadyl) in the insoluble product by electron spin resonance.

Significant reductions in the metal content of the filtered liquid product were obtained in coprocessing a variety of resid and coal combinations. The observed dependence of the metal (Ni + V) concentrations in the feed slurry is summarized in Figure 7. Similar demetalation effects were also found in experiments with Wyodak coal as indicated in Table 4.

The effect of additives other than coal on the coprocessing behavior of Maya ATB was investigated to gain further insight into the requirements for resid demetalation. As shown in Table 5, coprocessing Maya ATB with 30 wt% Illinois No. 6 coal or a high-surface-area activated carbon resulted in liquid products containing only 10-30 ppm vanadium. Similar results have been observed in coprocessing Maya ATB with cellulose chars.<sup>10</sup> In contrast, coprocessing Maya ATB with coal-derived pyrite, which exerts mild catalytic activity but has low surface area, resulted in an enhanced liquid yield but no significant demetalation above that obtained if only the resid is processed. Likewise, no significant demetalation of the liquid product was achieved by the addition of 30 wt% kaolin, which acts as a low-surface-area diluent. Also, the extent of demetalation of the liquid products in experiments with low concentrations of highly dispersed Mo catalyst is similar to that achieved without the added catalyst, although soluble product yields and coal conversion are considerably higher in the catalytic than the thermal-coprocessing experiments.

The experimental data in Table 5 suggest that a sufficient requirement for resid demetalation appears to be a high-carbonaceous insoluble surface area. There is no particular correlation of metals removal with liquid product yields or coal conversion.

The fate of organic vanadium was further investigated by semi-quantitative ESR procedures. Based on elemental analyses, more than 90% of the vanadium in the feed slurry is recovered in the heptane-insoluble product from coprocessing Maya ATB with 30 wt% Illinois No. 6 coal under the conditions used. The ESR analyses of the quadrivalent vanadium in the heptane insolubles from a variety of microautoclave coprocessing experiments are summarized in Table 6. There is no direct relationship between the amount of ESR-observable vanadyl and the degree of demetalation of the heptane-soluble product fractions. In the thermal microautoclave runs, the vanadium associated with the heptane insolubles remains largely in quadrivalent vanadium complexes even under a hydrogen atmosphere. The ESR spectra of the heptane insolubles from coprocessing Maya ATB with coal or activated carbon were remarkably similar. The addition of pyrite as a catalyst yielded a very lossy heptane-insoluble fraction that was not amenable to ESR analysis. Addition of a highly dispersed molybdenum catalyst resulted in a threefold decrease in ESR-observable vanadium in the heptane insolubles. It is reasonable to assume that the reduction reflects conversion of the organic vanadium into inorganic species (sulfides) or other species not observed by ESR. The ESR spectrum of the quadrivalent organic vanadium remaining in the heptane insolubles from the molybdenum-catalyzed run is similar to that obtained in the absence of an added catalyst.

## CONCLUSIONS

The observed thermal-coprocessing behaviour of petroleum resids is consistent with their limited compatibility with coal-derived materials and an inability to function as efficient hydrogen-transfer solvents. Under thermal-coprocessing conditions with Illinois No. 6 coal, the coal contribution to the heptane-soluble product was low for each of the three tested and varied in a linear manner with coal addition. This appears to be little more than a thermal extraction. There is evidence, particularly in coprocessing Illinois No. 6 with Maya ATB, for an enhanced yield of heptane solubles from the resid with coal addition. Except in coprocessing experiments with Maya ATB, calculated coal conversion to THF solubles fell with increasing coal addition. Under the conditions used, thermal-coprocessing results for Wyodak subbituminous and Illinois No. 6 bituminous coals were similar with respect to soluble product yields. Overall, the thermal-coprocessing experiments indicate the interaction between coal and petroleum resids is rather weak with respect to promoting the formation of liquid products.

The liquid product yields from thermal coprocessing of coal with untreated petroleum resids are too low to justify a completely non-catalytic approach to coprocessing. A limited improvement, particularly with respect to minimizing the yield of THF insolubles, can be realized by simply adding  $H_2S$  to the reducing atmosphere. However, the Maya ATB/Illinois No. 6 coal system responds favorably to addition of low concentrations of active, highly dispersed, unsupported transition metal catalyst. Although no systematic attempt was made to optimize conditions, only a few hundred parts per million of unsupported Mo appear to be necessary to obtain complete conversion to THF solubles and high heptane-soluble yields.

Under thermal-coprocessing conditions in a microautoclave reactor, conversion of organically complexed vanadium to inorganic sulfides or other ESR-unobservable forms occurs to only a limited extent. Minimal catalytic benefit owing to the presence of vanadium in the resid feedstock thus accrues in the absence of an added active hydrogenation catalyst.

Coal addition does facilitate demetalation of the heptane-soluble product from processing petroleum resids. The investigation of the requirements for demetalation in coprocessing indicates that the removal of the resid metals from the soluble product fractions is primarily associated with an interaction of the metal complexes and insoluble carbonaceous components rather than the coal mineral matter. The experimental results strongly suggest that an adsorptive mechanism is initially operative, followed by reactive incorporation of the complexed metal species into the carbonaceous insolubles and by extensive conversion of the metal to inorganic form under appropriate (catalytic) conditions. The primary function of coal is apparently to provide a surface upon which the vanadium species can deposit and undergo further regressive reactions.

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Table 1. Proximate and Ultimate Analyses of Feed Coals

	Illinois No. 6 ( <u>Burning Star</u> )	Wyodak ( <u>Clovis Point</u> )	Wyodak ( <u>Sarpy Creek</u> )
Proximate Analysis, wt%			
(As Received)			
Moisture	4.2	6.1	17.7
Volatile Matter	36.9	42.3	31.6
Fixed Carbon	48.2	40.8	38.8
Ash	10.7	10.8	11.9
Ultimate Analysis, wt%			
(Moisture Free)			
Carbon	70.2	64.4	62.9
Hydrogen	4.8	4.5	3.9
Nitrogen	0.9	1.0	0.8
Sulfur	3.1	0.9	0.9
Oxygen (Diff.)	9.9	17.7	17.0
Ash	11.1	11.5	14.5
Sulfur Forms, wt%			
Sulfate	0.03	0.02	
Pyritic	1.2	0.2	
Organic	1.9	0.7	

Table 2. Properties of Petroleum Resids

	North Slope VTB (950°F+)	Boscan ATB (650°F+)	Maya ATB (650°F+)
Ultimate Analysis (wt%)			
Carbon	86.1	82.5	84.5
Hydrogen	10.6	10.1	10.6
Oxygen	0.7	0.6	0.3
Nitrogen	0.6	0.7	0.5
Sulfur	2.0	5.6	4.0
Ash	<0.1	0.5	0.1
Ni (ppm)	60	120	70
V (ppm)	130	1300	370
°API	8.9	5.7	8.8
850°F- vol%			
ASTM D1160	--	19	30
Heptane Insols (wt%)			
ASTM D3279	4	20	20
$\bar{M}_n$ (VPO, pyridine, 80°C)	920	1250	720
$H_{ar}^*$	0.07	0.08	0.07
$f_a$	0.38	0.41	0.33



Table 3. Effects of H<sub>2</sub>S and Unsupported Mo Catalyst on Coprocessing Illinois No. 6 Coal (30 wt%) and Maya ATB (70 wt%)

Charge Atmosphere

H <sub>2</sub> (vol%)	H <sub>2</sub> S (vol%)	H <sub>2</sub> O(wt%) in Slurry	Cat.(wt%) in Slurry	Heptane- Soluble Yield (wt%)	%Coal Conversion to THF Sols
100	0	-	-	68	73
85	15	-	-	72	84
85	15	5	-	74	85
85	15	-	1.0	81	96
90	10	-	0.1	80	95
100	0	-	0.1	76	88

Note.      Temperature:      425°C  
              Residence Time:      1 hr  
              Charge Pressure:      1200 psig

Table 4. Observed Demetalation of the Filtered Liquid Products from Coprocessing Maya ATB (70 wt%) with Wyodak Subbituminous and Illinois No. 6 Bituminous Coals (30 wt%)

Coal	Coal In Feed Slurry (wt%)	Metals In Filtered Liquid Product (ppm)
Wyodak (Clovis Point)	20	50
	30	20
Illinois No. 6	20	60
	30	10

Note.      Temperature:      425°C  
              Residence Time:      1 hr  
              Charge Pressure:      1200 psig

Table 5. Effect of Various Additives in Processing Maya ATB

Petroleum Resid	Ill. No. 6 Coal (wt%)	Additive (wt%)	% Heptane Solubles in Product	Vanadium in Liquid (ppm)
Maya ATB	0	-	89	200
Maya ATB	30	-	68	20
Maya ATB	0	Deashed Thermal Resid (30%)	74	10
Maya ATB	0	Activated Carbon (30%)	61	30
Maya ATB	0	Coal-Derived Pyrite (30%)	71	210
Maya ATB	0	Kaolin (30%)	62	230
Maya ATB	30	-	72	20 <sup>a</sup>
Maya ATB	30	Mo (0.1%)	80	30 <sup>a</sup>

Note.      Temperature:      425°C  
              Residence Time:      1 hr  
              Charge Pressure:      1200 psig

<sup>a</sup> These runs contained 15 vol% H<sub>2</sub>S in the feed gas.

Table 6. Recovery of Organic Vanadium in Heptane Insolubles  
from Microautoclave Experiments

Feed Slurry Composition			Initial Reducing Gas Composition		Fraction of Feed Slurry Vanadium	
Petroleum Resid	Additive (30 wt%)	Catalyst (0.1 wt%)	H <sub>2</sub> (vol%)	H <sub>2</sub> S (vol%)	In Heptane Insolubles as Vanadyl (ESR)	In Heptane Sols (Elemental Analysis)
Maya ATB	Ill. No. 6	---	100	---	0.9 <sub>3</sub>	0.05 <sub>4</sub>
Maya ATB	Activated C	---	100	---	0.9 <sub>2</sub>	0.06 <sub>1</sub>
Maya ATB	Pyrite	---	100	---	0.01 (see text)	0.6 <sub>9</sub>
Maya ATB	Ill. No. 6	---	90	10	0.7 <sub>2</sub>	0.05 <sub>4</sub>
Maya ATB	Ill. No. 6	Mo	90	10	0.2 <sub>7</sub>	0.09 <sub>3</sub>
Boscan ATB	---	---	99	1	0.4 <sub>2</sub>	0.4 <sub>3</sub>
Boscan ATB	---	---	90	10	0.4 <sub>9</sub>	0.3 <sub>8</sub>
Boscan ATB	---	---	75	25	0.4 <sub>8</sub>	0.4 <sub>8</sub>
Boscan ATB	Ill. No. 6	---	90	10	0.8 <sub>2</sub>	0.08 <sub>8</sub>
N. Slope VTB	---	---	100	---	0.1 <sub>9</sub>	0.6 <sub>3</sub>
N. Slope VTB	Ill. No. 6	---	100	---	0.5 <sub>9</sub>	0.07 <sub>7</sub>

Note.      Temperature:      425°C  
              Residence Time:    1 hr  
              Charge Pressure:    1200 psig

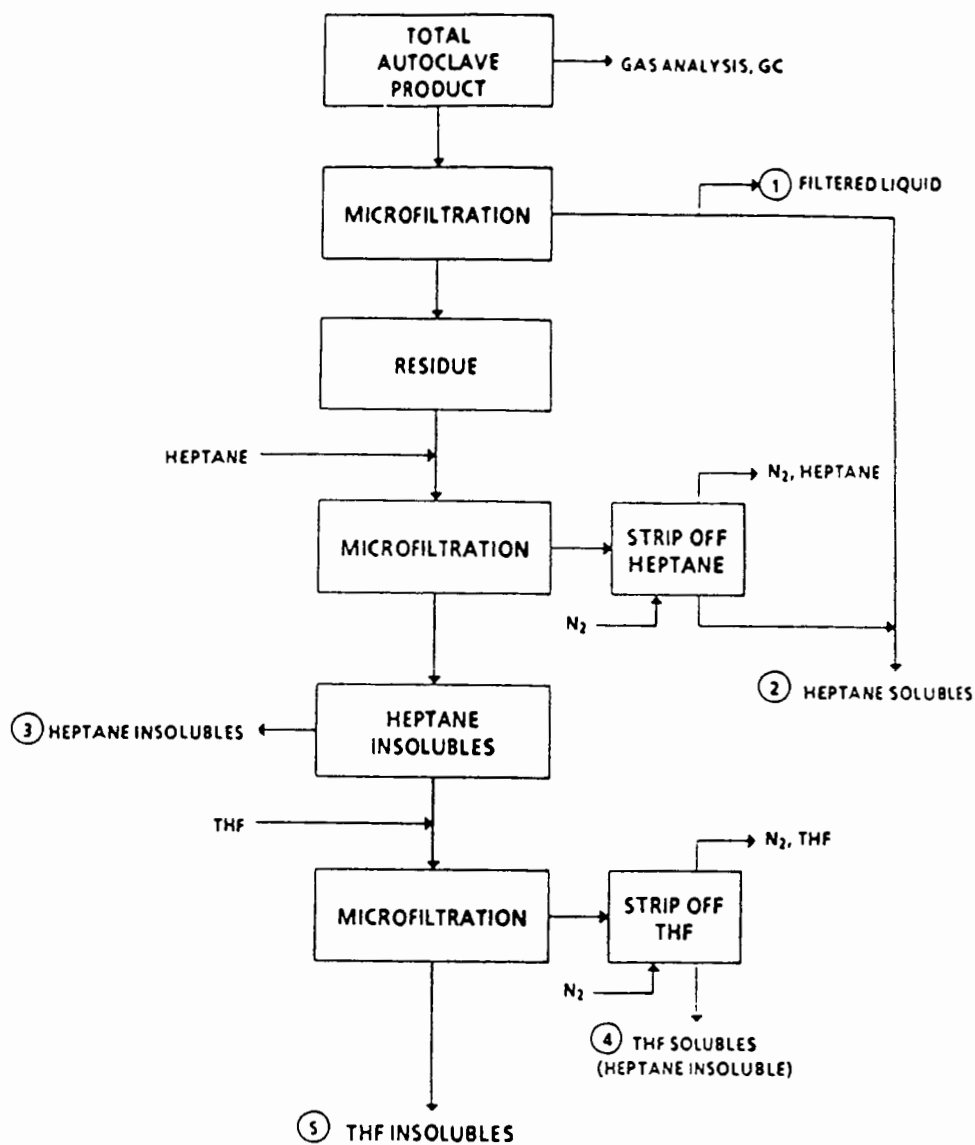


Figure 1. Microautoclave product work-up scheme.

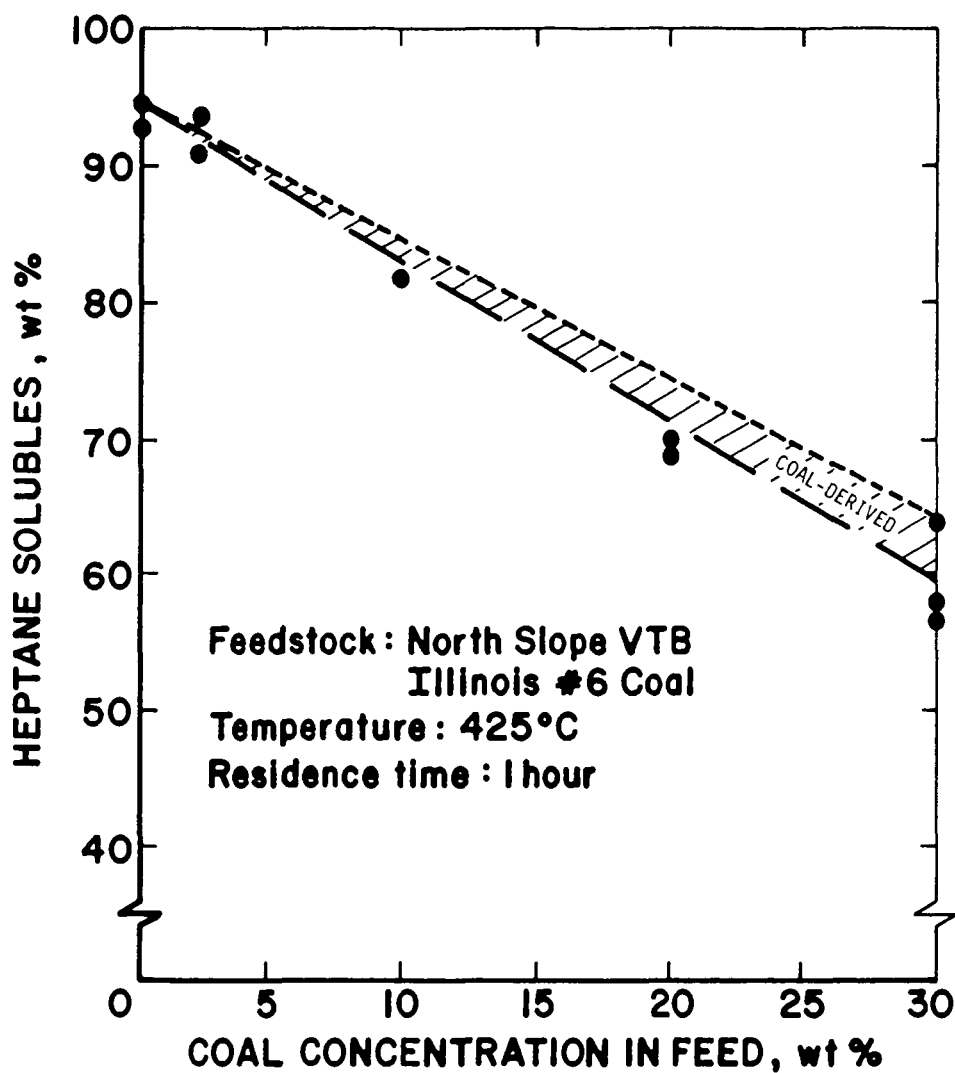


Figure 2. Effect of coal concentration on heptane-soluble yields in coprocessing North Slope VTB with Illinois No. 6 Coal.

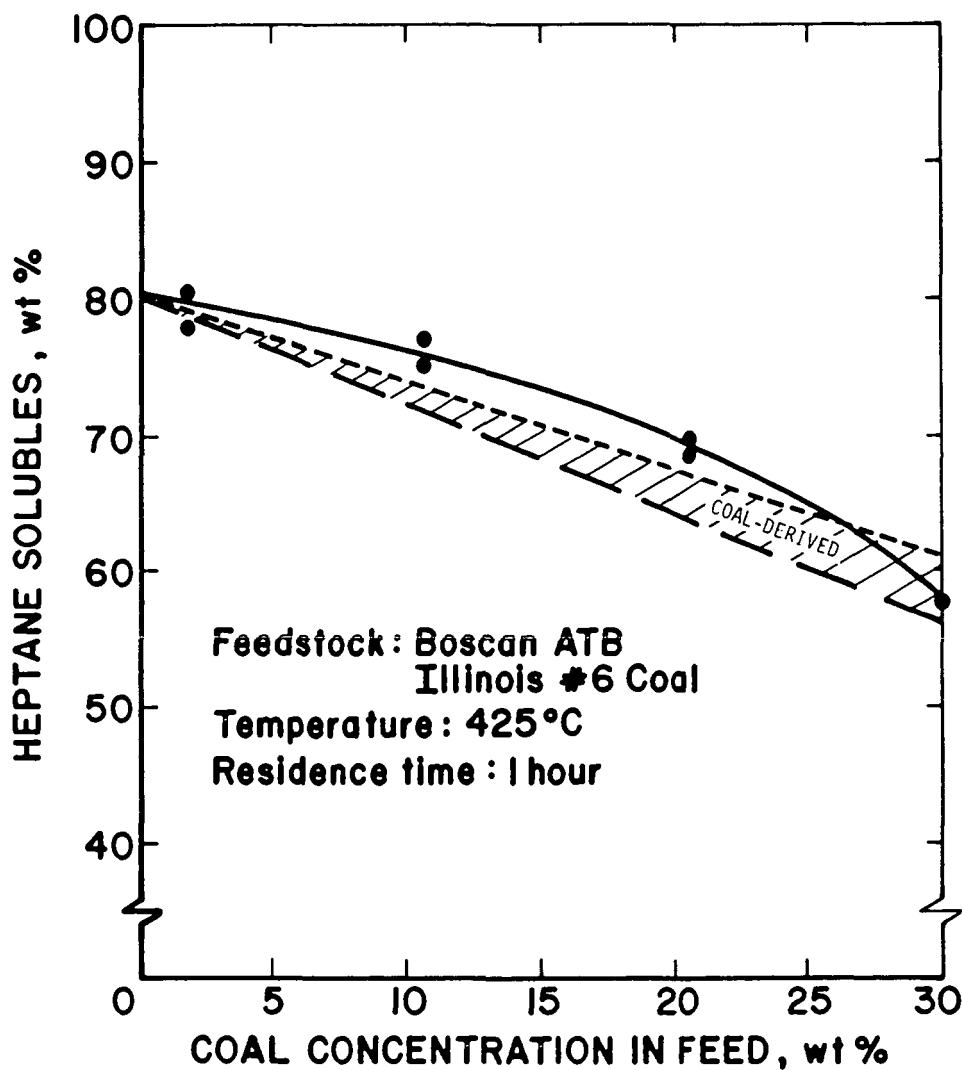


Figure 3. Effect of coal concentration on heptane-soluble yields in coprocessing BOSCAN ATB with Illinois No. 6 Coal.

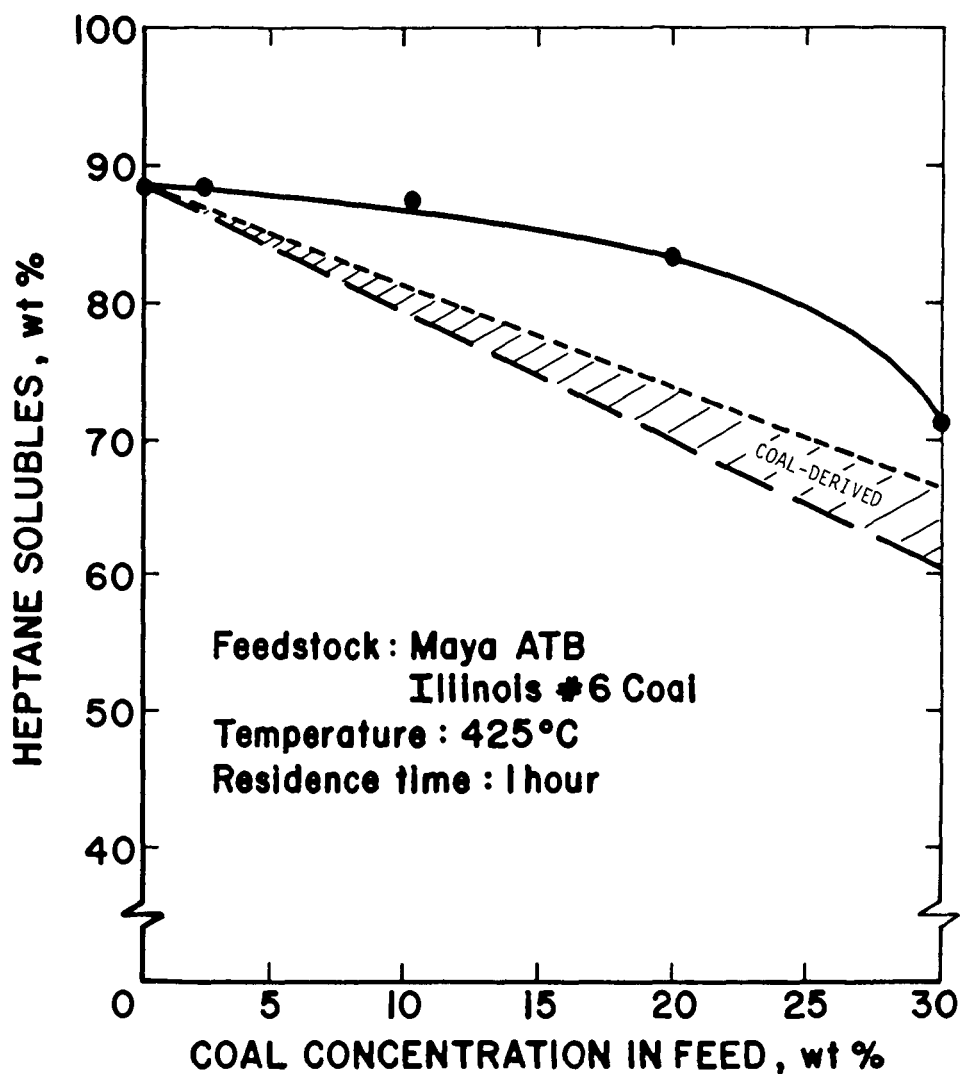


Figure 4. Effect of coal concentration on heptane-soluble yields in coprocessing Maya ATB with Illinois No. 6 Coal.

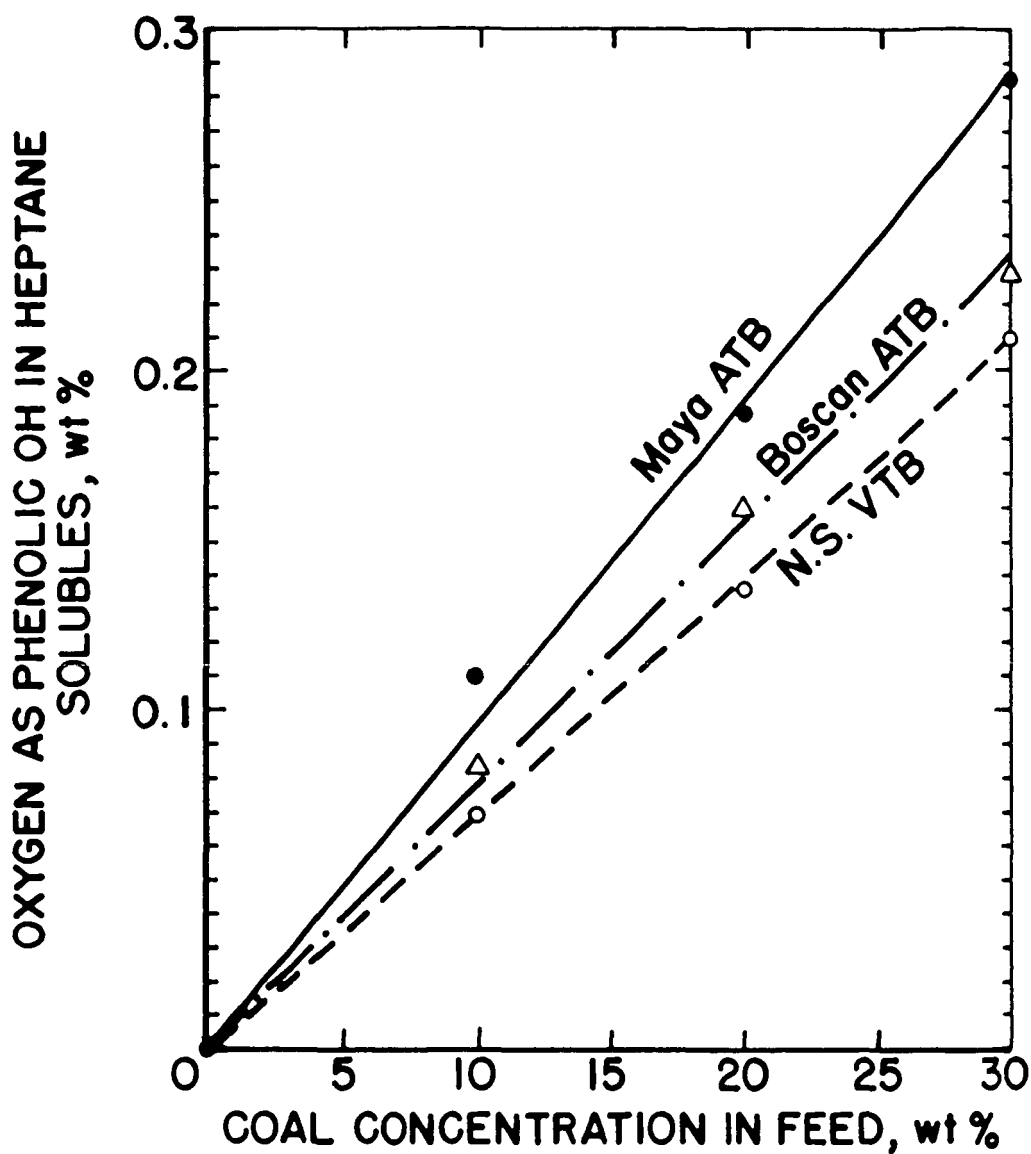


Figure 5. Effect of coal concentration on phenolic OH in the filtered liquid products from coprocessing petroleum residues with Illinois No. 6 Coal.



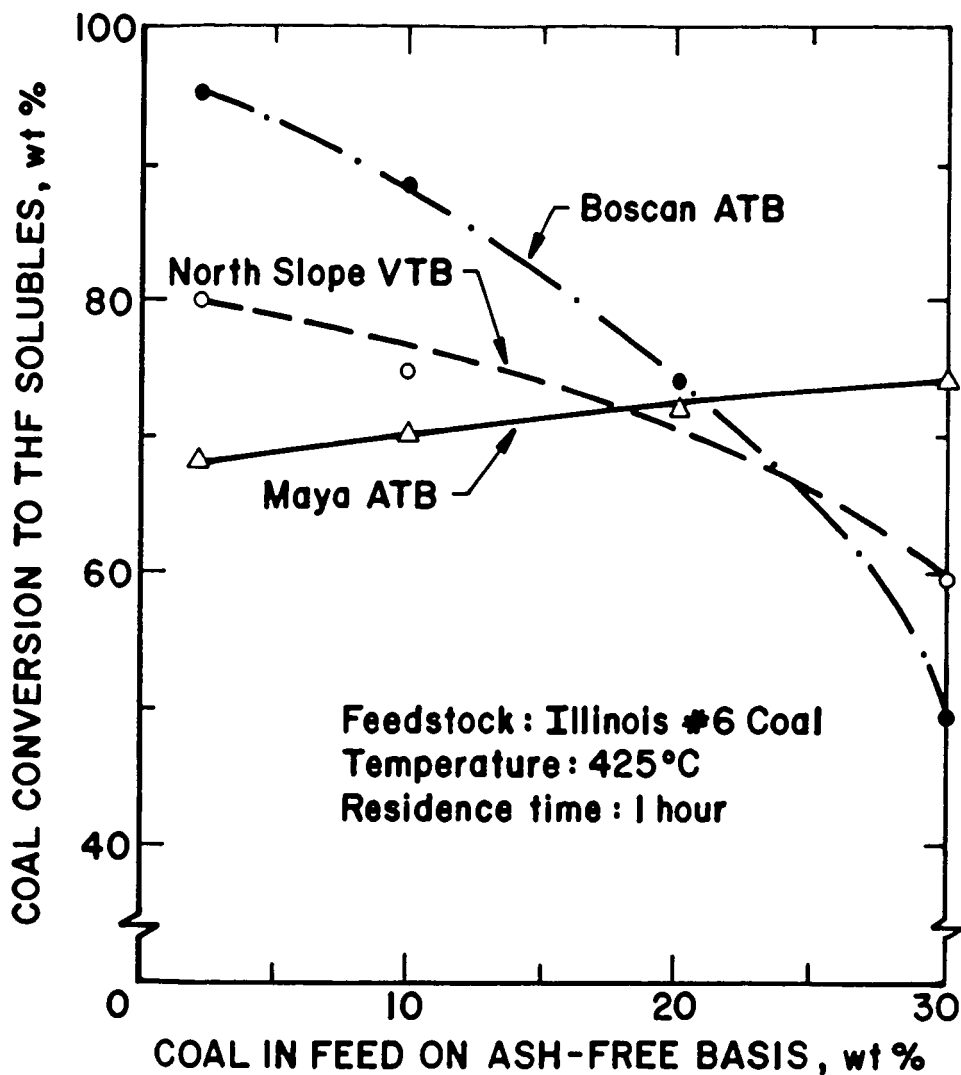


Figure 6. Effect of coal concentration on Illinois No. 6 Coal conversion to THF solubles in coprocessing with petroleum resids.

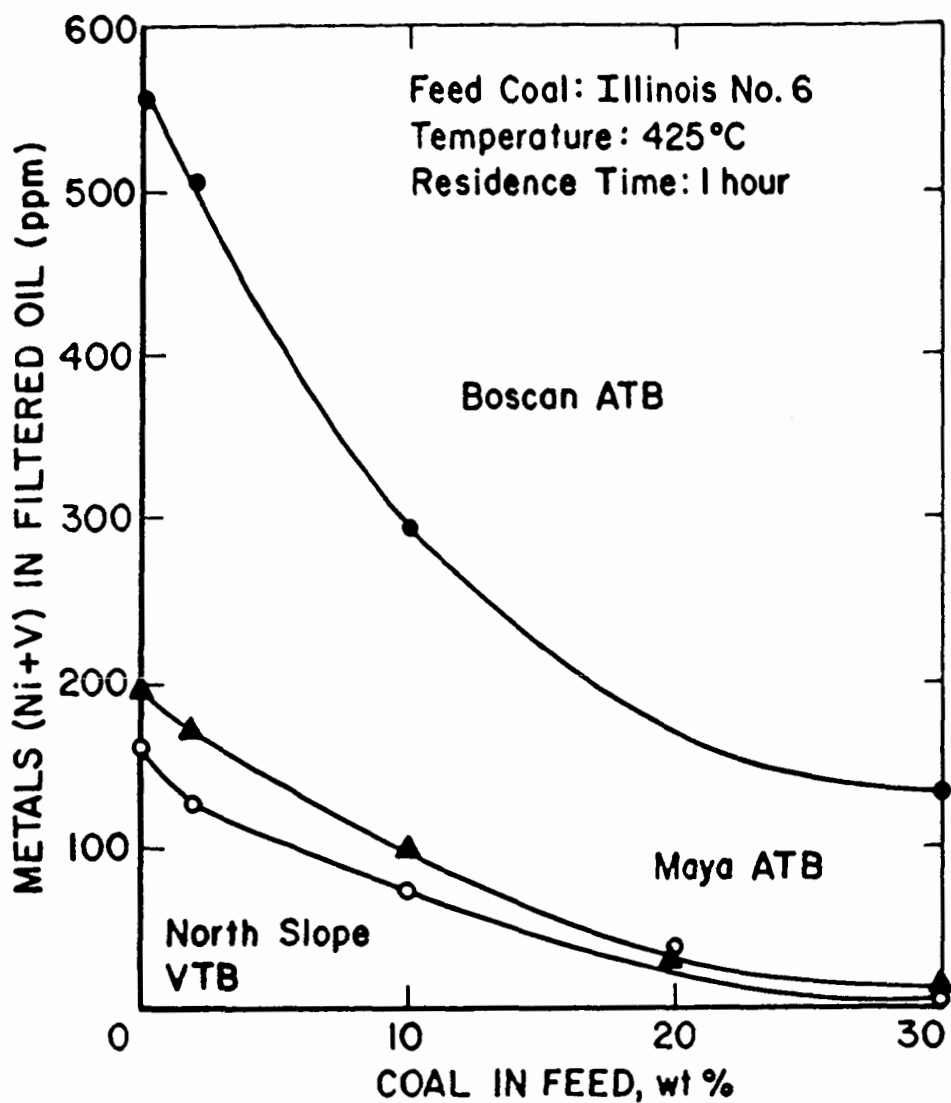


Figure 7. Effect of coal concentration on metals removal.